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TECHNIQUES FOR THE IDENTIFICATION OF SPECIFIC SOURCES OF AIRBORNE PARTICULATES

J. Hipfner, R.R. Martin, R. Moody, T. Lee, M. Guiliacci

Introduction

Source identification for airborne particulates is important both to insure effective remedial action and to assess potential health risks associated with specific air masses. Three methods for source identification are especially promising: elemental isotope distribution, trace element distribution and surface reactivity of the particles. A wide variety of experimental techniques are available at The University of Western Ontario including Secondary Ion Mass Spectrometry (SIMS), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR) and Ion Chromatography (IC). Other techniques are available such as Neutron Activation Analysis (NAA) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). We have confined our initial studies to the instruments readily available at The University of Western Ontario or at the Ontario Ministry of the Environment Laboratories. In addition we have sought to focus attention, where possible, on instrumentation which can be used in simple tests with a relatively unskilled operator. The main thrust of the report will be to examine the results obtained by IC and SIMS, the former is by far the easier technique. Some ICP-MS will also be reported

We have established that XPS and SEM were of limited utility without detailed study. XPS results are limited because the technique is surface sensitive (i.e. to two or three monolayers), the samples are prone to charging and are widely distributed on the filter surface. SEM has high detection limits ($\sim 1\%$) and with current instrumentation is not capable of detecting carbon, an element of special interest because it is abundant in atmospheric particles originating from combustion. FTIR showed the principle species in assemblies of particulate matter to be NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$, though organic functional groups such as carboxylates could be identified. The area will be pursued more vigorously in the future. NAA studies are underway but the technique is expensive, time consuming and produces low-level nuclear waste.

Finally early SIMS measurements show that there is insufficient material in a normal air sample to carry out isotopic analysis of the surface material. Accordingly we have chosen to study elemental distributions using SIMS imaging techniques. In addition we have chosen to assess the surface reactivity of air particulate material by measuring catalytic activity on the reaction: $\text{SO}_3^- \longrightarrow \text{SO}_4^-$.

This reaction was chosen because it has interesting environmental consequences (acid rain), may be indicator of the potential health effects of atmospheric particles and is easily followed using IC.

Experimental

1. Sample Collection

Sample were collected on glass fibre filters using high volume samples, by the Ontario Ministry of the Environment.

2. Trace Metal Analysis

Trace metal concentrations were obtained using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis. For each filter, two samples were made. The samples were prepared to determine the total metal concentration and the concentration at pH 5. The samples prepared for total metal determination was made by leaching a filter in 3% nitric acid for 30 minutes and filtration through a 0.8 μm Nucleopore filter. The samples prepared for metal determination at pH 5 were made by leaching the filter at pH 5 for 30 minutes and subsequent filtration through a 0.8 μm Nucleopore filter with stabilization in 0.5% nitric acid (100 μl of 35% nitric acid in 7 ml sample).

3. Ion Chromatography and the $\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}$ Reaction

The oxidation of S(IV) is pH dependent with the exact reactive species depending on the nature of the equilibrium system¹⁻⁶. However, it is generally agreed that the oxidation of S(IV) to S(VI) decreases as the aqueous phase becomes acidic⁷. Since the reaction is highly pH dependent, a buffer was used to control the pH. The buffer chosen was a 10 mM $\text{CH}_3\text{CO}_2\text{H}/\text{CH}_3\text{CO}_2^-$ buffer at pH 4.7, standardizing all the S(IV) oxidation tests.

The S(IV) oxidation test consisted of analyzing two planchets from one filter. Assuming the distribution of material on the filter was homogeneous, one piece of filter was used as the blank to determine the initial concentrations (or loadings) of the anions present (Cl^- , NO_3^- , SO_3^{2-} and SO_4^{2-}) on the filter and the other was used to test the S(IV) oxidation reactivity in a buffered solution. The blank sample was prepared by immersing the filter in 10.00 ml of distilled-deionized water (DDW). The second piece was immersed in a 0.01 M acetic acid/acetate buffer with a pH of 4.7 and the addition of SO_3^{2-} stock to approximately 15 ppm. The pH was measured with a Hanna Piccolo portable pH meter. The samples were allowed to react for approximately 24 hours in the dark.

The samples were analyzed by ion exchange chromatography (IC) to determine the concentration of the anions present. The liquid samples obtained from the filters were passed through a 0.8 μm Nucleopore filter to remove any large particles before injection into the ion exchange column. The ion chromatograph used was a hybrid consisting of a Dionex AS4 analytical column and a Dionex membrane suppressor as the eluent suppressor. The eluent used was 1.6 mM $\text{HCO}_3^-/\text{CO}_3^{2-}$ buffer at a flow rate of 2.2 ml/min. The eluting ions were detected with a Waters conductivity detector.

The S(IV) stock was prepared by dissolving Na_2SO_3 salt (BDH Chemicals). It was found there were significant amounts of Na_2SO_4 (7 to 15% by weight) already present, varying from stock to stock. In addition, it was found that the S(IV) stock solution was unstable decomposing at a rate of 10 to 15% per day. As a result, the S(IV) stock solution was made up fresh and calibrated by oxidizing the S(IV) and S(VI) with H_2O_2 and back calculated against sulfate standards.

4. SIMS Analysis

SIMS analysis was carried out using a CAMECA IMS 3f instrument with a O^+ primary beam rastered over a $400 \times 400 \mu\text{m}$ area while secondary ions for imaging were collected from a central circular spot 250 μm in diameter. The primary beam was at a current of 100 nA with 7.5 keV net energy. The filters selected for imaging were those which showed high catalytic activity in the SO_3^- oxidation reaction.

Results and Discussion

The results indicate that specific groups of filters show rapid SO_3^- oxidation to a degree which is significantly greater than that of other filter material. Generally, but not always, the reactive filters are shown by ICP-MS to be rich in metals, especially iron, manganese and nickel. In addition there are groups of filters that show significantly reduced levels of SO_3^- conversion. This latter effect may be due to organics which are preferentially oxidized by dissolved oxygen or to either organic or inorganic chelating agents (i.e. carboxylic acids or phosphates) which chelate metal ions in solution.

Metal ion and metal catalyzed oxidation of S(IV) have been observed to increase oxidation rates, but the exact nature of the interaction is not well understood⁽¹⁾. Such catalysts include iron, manganese, titanium, vanadium, copper and nickel⁽¹⁻⁴⁾. In addition, it is known that graphitic carbon can also catalyze S(IV) oxidation⁽⁸⁾. As well, S(IV) oxidation is believed to be light sensitive⁽⁹⁾.

SIMS imaging⁽¹⁰⁾ can be used to infer the chemical state of various elements on the filter surface. Thus Pb occurs in association with Br, probably the product of automobile exhaust containing Pb and Br from free radical scavengers added to the gasoline. Aluminosilicates can be readily recognized which are either crustal material (wind erosion) or the products of fossil fuel combustion. Interestingly P and F are often associated with the aluminosilicate material. This is suggestive of fertilizer (in the form of phosphate) while F may originate from $\text{Ca}_5(\text{PO}_4)_3\text{F}$ or as a byproduct of aluminium smelting.

Conclusions

The correlation between the metal concentrations and SO_3^- conversion shows that filters with the highest metal concentrations also have the highest conversion. This suggests that the oxidation of S(IV) in the chemical reactivity test in some of these filters is metal catalyzed. More significantly the wide variability in the reactivity of the filter material in contact with SO_3^- solutions shows that the reaction, in concert with IC, can be used to identify air masses which pose significant health hazards either by their direct effects or by the atmospheric chemistry they induce. As well, unusual activity may well be characteristic of the source of the particulate material.

The SIMS results show that ion imaging can be used to elucidate the chemistry of particulate material, which in turn serves as an indication of the source of the material.

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